UDC 677.047.62:666.189.212

CURRENT TRENDS IN THE DEVELOPMENT OF ORGANOSILICON COUPLING AGENTS FOR FIBERGLASS

N. M. Demina[1]

Translated from Steklo i Keramika, No. 7, pp. 18 – 21, July, 1999.

Current trends in the consumption of silane fibers by fiberglass manufacturing companies are discussed. New brands of organosilicon coupling agents offered by the leading world producers are described. The possibility of using silanes with different functional groups in the production of fiberglass materials with improved consumer properties is investigated.

The experience in fiberglass treatment with modifying compositions gained over a number of years suggests that coupling agents play an important role as a binding link at the interface between the reinforcing material and the polymer matrix [1]. The crucial difference between the organofunctional silanes used to modify thermosetting and thermoplastic matrixes consists in the nature of the organofunctional groups [2]. Russian manufacturers of fiberglass widely use vinyl- and methacryloxy-containing organosilicon dressing for materials containing polyester resins, and amino- and glycidioxy-derivative silanes for epoxy resins, their modifications, and thermoplastic materials.

Traditionally, the industry uses domestic products (Table 1). Over the last years, analogous silanes produced by different companies, such as Witco (USA), Degussa-Huls (Germany), and Dow Corning (USA) have gained wide acceptance. To date, the production of trimethacryloxypropyltrimethoxysilane is nonexistent in Russia, and the commonly used product is A-174 made by Witco. At the end of the 1980s, production of methacryloxy-containing silanes was started in Moscow (the Penta company). The co-condensate and bicondensate are polyfunctional coupling agents which have a universal effect with respect to different types of matrixes and mineral fillers and impart a wide spectrum of properties to the material (Table 1).

The leading world producer of silanes, the Witco OrganoSilicons Group, offers the products Silguest which can react with different organic and inorganic materials. *The universal capabilities of the coupling agents are corroborated in the expanding areas of their application: filler treatment; fiberglass; adhesives; coatings; oil refining; polymer cross-linking; foundry; printing inks, rubber, and elastomers; sealing materials; textile production. Among the new coupling agents (Table 2), the dialkoxysilanes merit particular attention.*

The treatment of the filler surface with modifiers does not accomplish 100% binding of Si – OH groups, since it is assumed that all atoms near the surface are hydrolyzed to silanols. Thus, in trialkoxysilanes, the most probable is the formation of two siloxane bonds, and at the same time, the remaining Si – OH group acts as the water sorption site and has a strong effect on the hydrolytic stability of the bond [3]. The "excess" alkoxy groups retard the course of the reactions, since they fill a substantial part of the surface by hydrophylic substitutes. The Silguest® products A2171 (vinylmethyldimethoxysilane) and A-2120 (N(β-aminoethyl)-γ-aminopropylmethyldimethoxysilane) are widely tested in the production of adhesives, sealers, and latex coatings, and are of interest for use on fiber surface.

The organofunctional silanes CoatOSil® 1757 (Y-11857) and CoatOSil® 1706 (Table 2) each contains three isopropoxy groups. The structure of these silanes provides for unusually high stability of aqueous compositions containing these coupling agents. The aqueous compositions which contain the CoatOSil® 1706 silane preserve their stability and efficiency after 1 year of storage (according to the data of the Witco company).

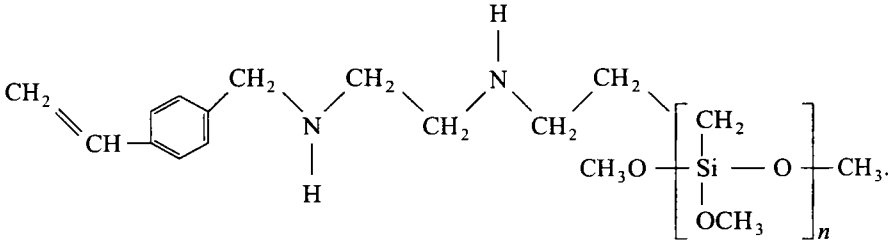
The Y-9669 organofunctional silane combines the phenyl and the amine function in one molecule. This makes it possible to expect high efficiency for various filled and reinforced polymer systems, especially for materials exposed to the effect of high temperatures. This agent is recommended for such polymers as urethanes, epoxides, acrylates, and phenol resins, which should adhere to inorganic substrates, for instance, glass, metals, fiberglass, and disperse fillers. According to the Witco data, the strength parameters of the phenol resin/fiberglass composite with the participation of the Y-9669 silane after long-term exposure to in-

[1] TERM Science and Production Company (subsidiary of NPO Steklopastik), Russia.

creased temperature and moisture effects are sufficiently high, which is evidence of the higher efficiency of Y-9669 compared to silane A-1100 in the high-temperature aging of phenol fiberglass.

The second largest producer of organo-derivative silanes is the Sivento Chemie GmbH of the Degussa-Huls concern. The deciding factor for the quick introduction of coupling agents bearing the Dynasilan® trademark at Russian and CIS fiberglass works is their lower cost, as compared to the Witco products. Sivento produces the following dialkoxysilanes: Dynalsylan® 1505 (triaminopropylmethyldiethoxysilane) and Dynasylan® 1411 (N-(diaminoethyl)triaminopropylmethyldimethoxysilane) [4]. The company offers vinyl-containing oligosiloxanes with degree of polymerization $n = 1 - 3$ with methoxy functions, namely, Dynasylan® 6490, and with ethoxy functions (Dynasilan 6498) which are the most promising for organic polymers with peroxide-containing modifiers.

Sivento offers promising cation diaminosilanes for treatment of fiberglass fabric. These are products with the common formula



The commercial forms are Dynasylan® 1172 (50% solution in methanol) and Dynasilan® 1372 (50% solution in a mixture of methanol with ethanol). The specified products are quickly dissolved in acidified water, and the silanol solutions are stable for 7 days and more. These coupling agents are especially active with respect to mineral fillers and epoxy resins. Coupling agents with a similar organofunctional group complex are offered in the Russian market by the Dow Corning company. The styryldiaminosilanes dissolved in methanol (40% active substance) have the trade names Z-6032 and Z-6224 [5].

Particular attention in the development of lubricants for fiberglass is paid to the toxicity of all components of the composition. Due to the high production rate of glass fiber strands, the products tend to form stable aerosol clouds which negatively affect the mucous membranes, upper respiratory organs, and skin of the operators.

The most promising with respect to production safety are aqueous solution of organofunctional silanes. Thus, the Witco offers aqueous solution of aminoalkoxysilicon of the formula $(H_2NCH_2Ch_2CH_2SiO_{1.5})_n$ (brand A-1106). The product is alcohol-free both as a solvent and as a hydrolysis

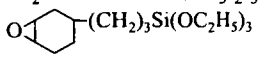
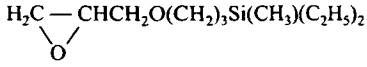
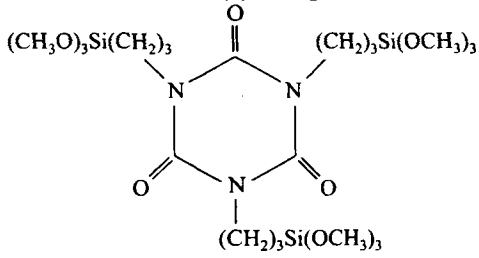
TABLE 1

Chemical formula of product	Trademarks and brands			
	in Russia	Witco Company	Degussa-Huls Company*	Dow Corning Company
$CH_2 = CHSi(OC_2H_5)_3$	VTES	A-151	DS VTEO	–
$CH_2 = CHSi(OC_2H_4OC_2H_5)_3$	GVS-9	A-172**	DS VTMOEO**	Z-6082**
$CH_2=C(CH_3)OCO(CH_2)_3Si(OCH_3)_3$	–	A-174	DS MEMO	Z-6030
$H_2N(CH_2)_6NHCH_2Si(OC_2H_5)_3$	AGM-3	A-1120**	DS DAMO**	Z-6020**
$(C_2H_5)_2NCH_2Si(OC_2H_5)_3$	ADE-3	–	–	–
$H_2N(CH_2)_3Si(OC_2H_5)_3$	AGM-9	A-1100	DS AMEO	–
$H_2C-CHCH_2O(CH_2)_3Si(OC_2H_5)_3$ (O)	ÉS-1	A-187**	DS GLYMO**	Z-6040**
$CH_2=COCOCH_2CHCH_2NH(CH_2)_3Si(OC_2H_5)_3$ (CH_3, OH)	Penta 62 (co-condensate)	–	DS HS2929**	–
$(CH_2=COCOCH_2CHCH_2)_2N(CH_2)_3Si(OC_2H_5)_3$ (CH_3, OH)	Penta 61 (co-condensate)	–	–	–

* DS) Dynasylan.

** The product structure is very close to the presented formula.

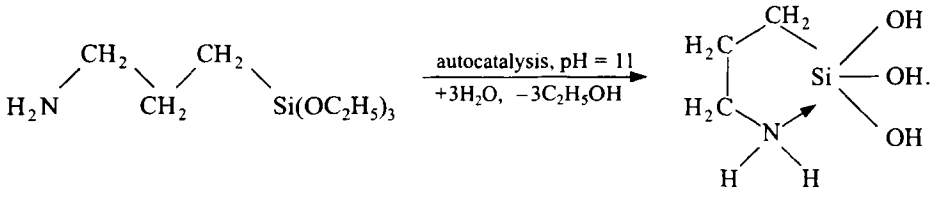
TABLE 2

Functional group	Chemical formula of product	Trademark
Methacryloxy	$CH_2=C(CH_3)OCO(CH_2)_3Si(OC_2H_5)_3$	Y-11878
	$CH_2=C(CH_3)OCO(CH_2)_3Si(OCH(CH_3)_2)_3$	CoatOSil® 1757 Y-1187
Sulfur	$(C_2H_5O)_3Si(CH_2)_3S_4(CH_2)_3Si(OC_2H_5)_3$	A-1289
	Polysulfidesilane	RC-2
Dialkoxy	$H_2N(CH_2)_2NH(CH_2)_3Si(CH_3)(OCH_3)_2$	A-2120
	$CH_2=CHSi(CH_3)(OCH_3)_2$	A-2171
Amino	$H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$	A-1130
	$HN((CH_2)_3Si(OCH_3)_3)_2$	A-1170
	$H_2N(CH_2)_3Si(OC_2H_5)_3$	A-1110
	$(H_2N(CH_2)_3SiO_{1.5})_n$	A-1106NS142
	$C_6H_5NH(CH_2)_3Si(OCH_3)_3$	Ó-9669
Vinyl	–	RC-1
	$CH_2=CHSi(OCH(CH_3)_2)_3$	CoatOSil® 1706
Epoxy		CoatOSil® 1770
		Y-15078
Ureido	$H_2NCONH(CH_2)_3Si(OCH_3)_x(OC_2H_5)_{3-x}$	A-1160*
	$H_2NCONH(CH_2)_3Si(OCH_3)_3$	Y-11542
Alkyl	$C_8H_{17}Si(OC_2H_5)_3$	A-137
	$CH_3Si(OC_2H_5)_3$	A-162
Isocyanate	$OCN(CH_2)_3Si(OC_2H_5)_3$	A-1310
		Y-11597

* 50% solution in methanol.

product, is not inflammable, can be easily diluted with water, and is suitable as an additive to water-soluble and water-emulsifying compositions. This product is recommended as a coupling agent for fiberglass and fiberglass fabric with acrylic, epoxy, and phenol binders.

Degussa-Huls offers a whole range of water-soluble silanes. Dynasylan® 1151 is a 40% solution of aminopropyltriethoxysilane in water which is stable for at least 1 year and exists, according to its developers, in the form of the hydrolyzate:



Coupling agents in which the hydrolysis of the alkyl groups has been completed and the condensation of the silanol groups has not yet begun are thought to be the most suitable for filler surface treatment [1.6]. The use of the Dynalasan® 1151 coupling agent makes it possible to obtain well-oriented layers with increased cohesive strength on the filler surface. The treatment of non-porous smooth fillers, such as fiberglass, with a highly diluted silane solution will produce coupling layers of the most regular structure.

The Dynasylan® HS silanes (Table 2) are a new class of environmentally pure coupling agents which are instantly and completely soluble in water and have the same or better cross-linking activity as the industrially used 100% monoorganofunctional coupling agents.

TABLE 3

Functional group	Silane mass content, %	Trademark*
Amino/alkyl	40	DS® HS 2627
Diamino/alkyl	40	DS® HS 2776
Amino/vinyl	40	DS® HS 2781
Amino/vinyl	80	DS® HS 2907
Amino/alkyl	60	DS® HS 2909
Epoxy	40	DS® HS 2926
Amino/methacryloxy	50	DS® HS 2929

* DS®) Dynasylan®.

Of great interest is also the Dynasylan® F8261 product (tridecafluoroctyltriethoxysilane) produced by Sivento, whose use in slight quantities (below 2 wt.%) radically modifies the surface, imparting chemical and thermal stability and UF radiation resistance to the surface [4].

Apparently, the role of the coupling agent in compositions used for fiberglass treatment consists in the formation of compounds which are strongly fixed on the filler surface and increase its activity with respect to the polymer, since they contain functional groups that can react chemically with the binder molecules [1, 2, 3, 6, 7]. The authors of [4] believe that there is a limit to the efficiency of the monofunctional trialkoxysilanes. Correctly constructed polyfunctional silanes can extend the efficiency limits of silane coupling agents, which will allow for an increased level of physicomechanical and technological properties in glass-reinforced composites.

REFERENCES

1. E. Plueddemann (ed.), *Composite Materials*, Vol. 6, *Surface Interface in Polymer Composites*, New York, Academic Press (1974).
2. K. L. Locwenstein, *The Manufactoring Technology of Confinios Glass Fibers*, Elsevier, Amsterdam (1995).
3. E. P. Plueddemann, *Silane Coupling Agents-2*, Plenum Press, New York – London (1992).
4. *Lieferprogramm. Silicone und Silane*, Sivento (1998).
5. "Dow Corning®, Z-6224 Coupling Agent," *Information about Coupling Agents*, Dow Corning (1998).
6. A. I. Makhal'skii, "Organofunctional coupling agents in filled polymer systems," *Itogi Nauki Tekhn. Ser. Khim. Tekhnol. Vysokomol. Soed.*, **19**, 151 – 222 (1984).
7. Yu. S. Lipatov, *Interphase Phenomena in Polymers* [in Russian], Naukova Dumka, Kiev (1980).